

Abstract of the Thesis

Title of the Ph.D. Thesis: Interaction between Polyelectrolytes and Surface Active Ionic Liquids

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Registration No.: 14RS205120001 dated 18.03.2016

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With a view to elucidate the polyelectrolyte-surface active ionic liquid interactions, the present dissertation aims to investigate the influence of polyelectrolytes on the aggregation behaviour of surface active ionic liquids in aqueous solutions using different experimental techniques.

For the study, we selected two negatively charged polyelectrolytes - sodium carboxymethylcellulose (NaCMC) and sodium polystyrenesulfonate (NaPSS), and two surface active ionic liquids - 1-decyl-3-methylimidazolium chloride ($C_{10}\text{MeImCl}$) and 1-hexadecyl-3-methylimidazolium chloride ($C_{16}\text{MeImCl}$). Four different experimental techniques, namely, conductometric, tensiometric, osmometric and spectrofluorimetric techniques were employed to explore and elucidate the nature of interactions in the investigated polyelectrolyte-surface active ionic liquid solutions. In particular, NaCMC- $C_{10}\text{MeImCl}$, NaCMC- $C_{16}\text{MeImCl}$, NaPSS- $C_{10}\text{MeImCl}$, NaPSS- $C_{16}\text{MeImCl}$ mixed solutions were investigated.

The measured electrical conductances on aqueous NaCMC and NaPSS have been analyzed using the scaling description for the configuration of a polyion chain. Evaluation of the fractions of free counterions, free energies of counterion-condensation, the ratios of the mobility of the polyion to that of the counterion, the polyion transference numbers, and the coefficients of monomer-solvent friction provided important information as to the counterion-condensation behavior in these solutions.

Studies on aqueous NaCMC- $C_{10}\text{MeImCl}$, NaCMC- $C_{16}\text{MeImCl}$, NaPSS- $C_{10}\text{MeImCl}$, NaPSS- $C_{16}\text{MeImCl}$ solutions indicated the formation of surface-active complexes consisting of surfactant monomers bound to the polyion backbone, and non-surface active necklace-like polyion-micellar aggregates, and free $C_{10}\text{MeImCl}$ and $C_{16}\text{MeImCl}$ micelles in these solutions.

The alkyl chain length of the surface active ionic liquid molecules investigated has a profound influence on their aggregation behaviour in absence as well as in presence of NaCMC or NaPSS. Micellization of $C_{10}\text{MeImCl}$ and $C_{16}\text{MeImCl}$ was found to become

somewhat less spontaneous upon addition of NaPSS or NaCMC at any given temperature, and that the spontaneity of micellization decreases as the amount of added polyelectrolyte increases. In presence of the polyelectrolytes, however, the micellization becomes more spontaneous upon an elevation of temperature. The bulk structural property of the investigated aqueous polyelectrolyte-surface active ionic liquid solutions was found to be deviated appreciably from that of the pure water, particularly in solutions containing $0.0005 \text{ mol.L}^{-1}$ of NaCMC or NaPSS.

The present work provided important information on the polyelectrolyte-surface active ionic liquid solutions in particular, and polyelectrolyte-surfactant solutions in general.